

Familiarization and Detection of Green Monopropellants

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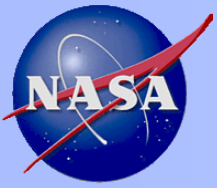
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Outline

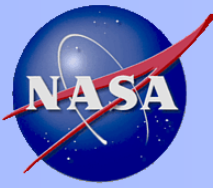
- **Background**
- **Detection Methods**
 - **Hydroxylammonium Nitrate (HAN) – AF-M315E**
 - **Ammonium Dinitradmide (ADN) – LMP-103S**
- **Safety Considerations**
- **Conclusions**



Background

- **“Green” Monopropellants AF-M315E and LMP-103S**
 - Reduced Toxicity and Increased Performance compared to Hydrazines
 - Hydroxylammonium Nitrate (HAN) based Monopropellant (AF-M315E)
 - Developed by US Air Force Research Laboratory
 - Ammonium Dinitradmide (AND) based Monopropellant (LMP-103S)
 - Developed by ECAPS (Swedish Space Corporation)
 - Little is known about the safety and handling of “Green” Monopropellants at NASA Kennedy Space Center (KSC)

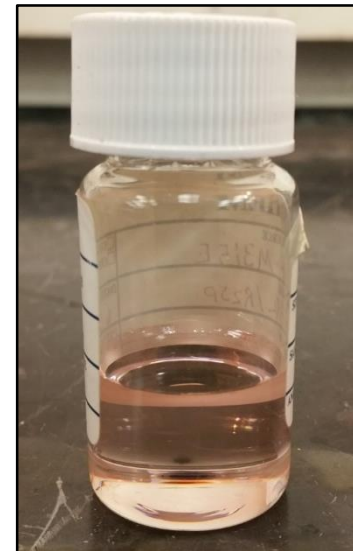
- **Familiarization and Detection of Green Monopropellants**
 - Project goals
 - Evaluate detection methods for HAN- and ADN-based monopropellants
 - Develop detection kits for HAN- and ADN-based monopropellants
 - Become familiar with HAN/ADN properties
 - Funded by NASA Kennedy Space Center Funds



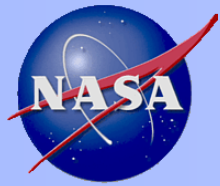
Hydroxyammonium Nitrate – HAN

- **Primary component of AF-M315E monopropellant**
 - 42% Hydroxyammonium Nitrate (HAN)
 - Negligible vapor pressure
 - Eliminates traditional monitoring techniques
 - Requires physical contact with detection method

- **“Green” Monopropellant AF-M315E**
 - Produced by Air Force Research Laboratory (AFRL)
 - Negligible vapor pressure eliminates traditional monitoring techniques
 - NASA Technology Demonstration Mission (TDM)
 - Awarded to Ball Aerospace & Technologies Corporation
 - Green Propellant Infusion Mission (GPIM) is scheduled for 2016
 - Participant in F-16 Emergency Power Unit (EPU) test conducted at NASA Marshall Space Flight Center (MSFC)



AF-M315E Lot #33



Detection Methods Evaluated

- **Colorimetric**

- Passive method
- Wide range of possible color reagents
- May be useful for containment/cleanup



Hydrazine Dosimeter Badge

- **COTs Sensors**

- **Vapor Sensors**

- Ammonia-based sensors
- Actively-pumped and diffusion-based systems

- **Liquid Detection**

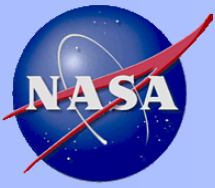
- Detect Conductive Liquids
 - Water and/or Chemical



RLE Technologies SeaHawk
LD310 Single Zone Monitor



Hydrazine Vapor Monitor



COTS Sensors: Liquid Detection

- **RLE Technologies Chemical Sensing Cable**
 - Detects a variety of conductive chemical liquids
 - Previously untested using the “Green” Monopropellant AF-M315E
 - Chemically Resistance to several acids in accordance to ASTM D543
 - Operating Temperature Range: -40° to 85°C
 - Available in standard or custom lengths
 - Constructed from thermally bonded polymer coated carrier
- More information can be found at
 - <http://rletech.com/our-products/sensing-cables/chemical-sensing-cable/>



RLE Technologies Chemical Sensing Cable



RLE Technologies SeaHawk LD310 Single Zone Monitor

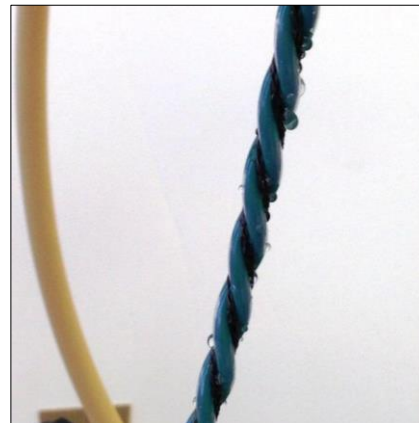


Liquid Detection – Test Results

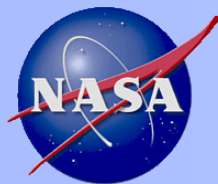
- The initial RLE Technologies Chemical Sensing Cable sensor tests were performed using the following aqueous solutions (for baseline purposes): 18 MΩ water, 0.5% sodium chloride solution, 0.1 M ammonium hydroxide solution, and 0.1 M sodium hydroxide solution.
- Results of this testing indicate that the RLE Chemical Sensing Cable is capable of detecting AF-M315E within 10 seconds of submersion, regardless of affected area even at a surface coverage of 1".
 - Deionized H₂O produced similar results, suggesting that the RLE Chemical Sensing Cable would not be useful in an environment in which moisture would be an issue, as this may lead to false positives.



Submersion Test of RLE Chemical Sensing Cable, AF-M315E

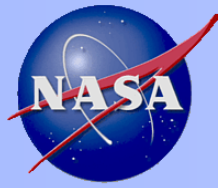


Close-up of RLE Chemical Sensing Cable Drip Test (18 MΩ Water).

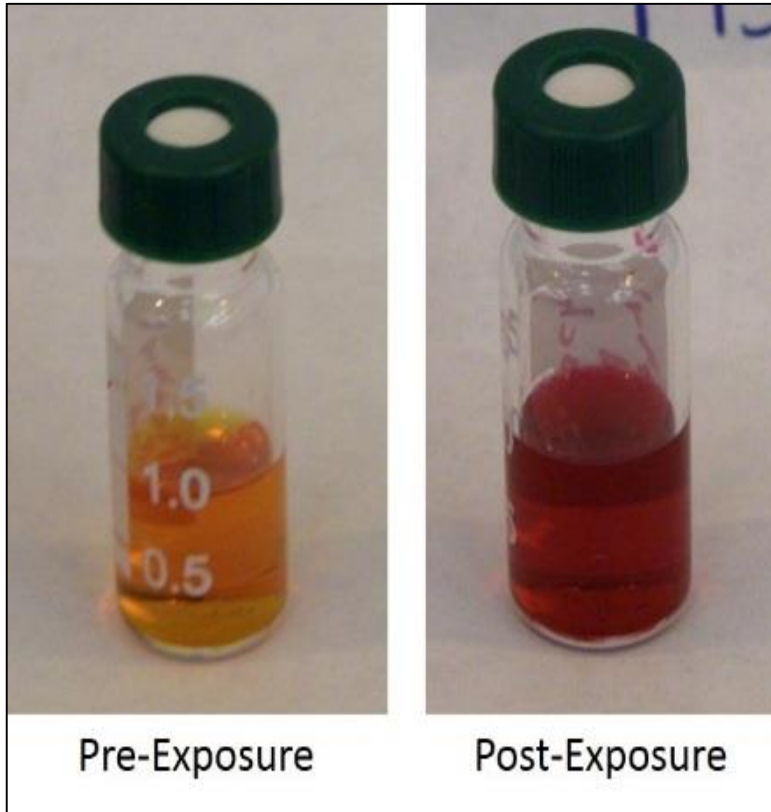


Colorimetric: Reagents Evaluated

Indicator	Properties
Acros Universal pH Indicator Solution	Initial color is green. Color changes: pH 4.0 (red), pH 4.5 (orange-red), pH 5.0 (orange), pH 5.5 (orange-yellow), pH 6.0 (yellow), pH 6.5 (yellow-green), pH 7.0 (green), pH 7.5 (green, slightly blue), pH 8.0 (green-blue), pH 8.5 (blue-green), pH 9.0 (blue)
Bromocresol Green (Basic)	Color change: pH 4.5 – 5.5
Bromocresol Purple (Basic)	Color change: pH 5.4 – 6.8
Bromothymol Blue (Basic)	Color change: pH 6.0 – 7.6
Methyl Red (Basic)	Color change: pH 4.8 – 6.0
Vanillin	Changes color when reacted with various reagents
VWR Universal Indicator	Initial color is green. Color changes: pH 4.0 (red), pH 5.0 (orange), pH 5.5 (orange-yellow), pH 6.0 (yellow-orange), pH 6.5 (yellow), pH 7.0 (green), pH 7.5 (green-blue), pH 8.5 (blue), pH 9.0 (blue-indigo), pH 9.5 (indigo), pH 10.0-11.0 (violet)
Yamada Universal Indicator (Acidic)	Initial color is red. Color changes: pH 4 (red), pH 5 (orange), pH 6 (yellow), pH 7 (green), pH 8 (blue), pH 9 (indigo), pH 10 violet
Yamada Universal Indicator (Neutral)	Initial color is green. Color changes: pH 4 (red), pH 5 (orange), pH 6 (yellow), pH 7 (green), pH 8 (blue), pH 9 (indigo), pH 10 violet



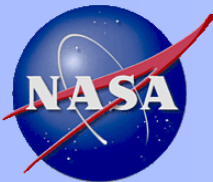
Methyl Red – Solution/Wipe Tests



Methyl Red (Stock)



Methyl Red (Basic) – a) post-exposure, b) pre-exposure, c) DI H₂O



Methyl Red (Basic): Absorbent Materials

- **Variety of materials tested**



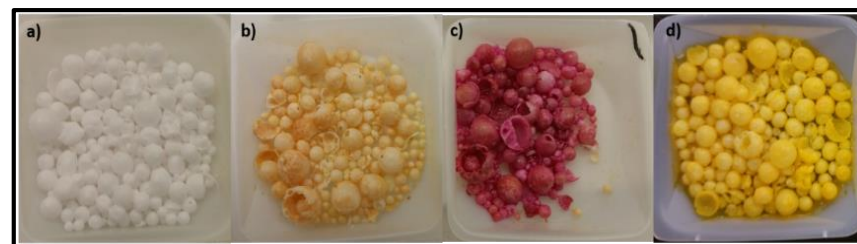
Activated Alumina Test – a) blank, b) pre-exposure, c) post-exposure (AF-M315E) and d) post-exposure (DI H₂O)



Fisher Filler Test – a) blank, b) pre-exposure, c) post-exposure (AF-M315E) and d) post-exposure (DI H₂O)



3M Filler Test – a) blank, b) pre-exposure, c) post-exposure (AF-M315E) and d) post-exposure (DI H₂O)

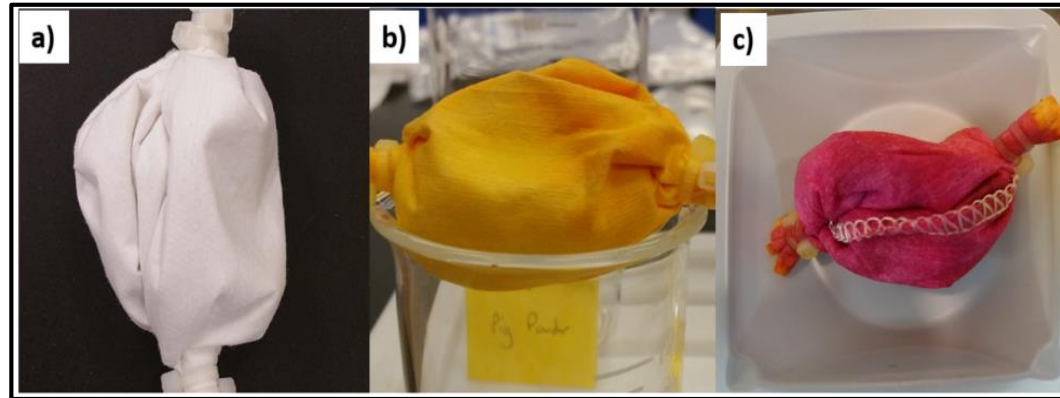


Alumina Bead Test – a) blank, b) pre-exposure, c) post-exposure (AF-M315E) and d) post-exposure (DI H₂O)



Methyl Red (Basic): Absorbent Socks

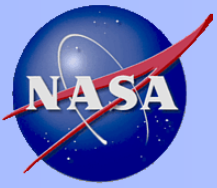
- The final phase of testing for the development of a detection system for HAN/AF-M315E was performed by preparing different test samples using the most promising candidates from the absorbent materials testing and encasing them within a compatible material.
 - Activated alumina, pig powder, and 3M Filler material were selected for testing
- For the exposure test, 5 ml of AF-M315E monopropellant was placed in a weigh boat and the “sock” to be tested was placed directly on the commodity.
- After approximately one hour, the samples were removed from the weigh boats to determine if any monopropellant remained unabsorbed.



Fisher Filler Test – a) blank, b) pre-exposure, c) post-exposure (AF-M315E)

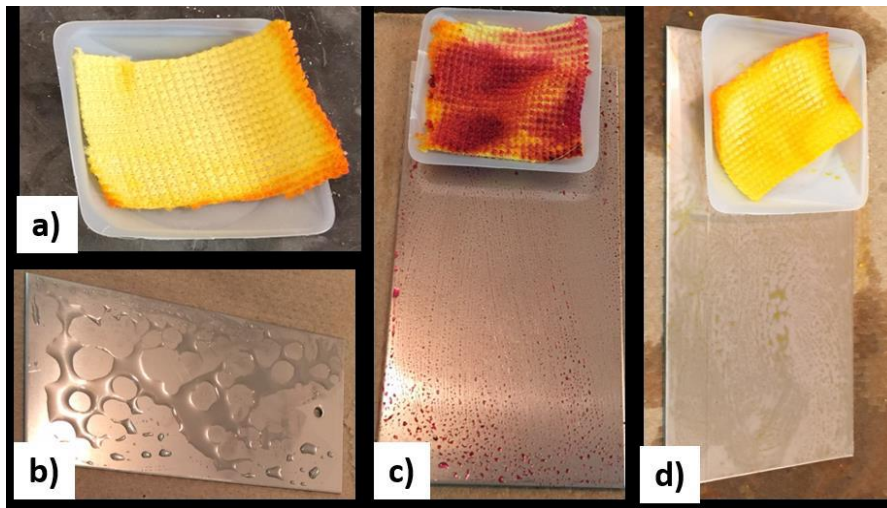


Fisher Filler Test – a) pre-exposure, b) 40 mL AF-M315E, c) 40 mL DI H₂O



Wipe Test – AF-M315E

- Using the Methyl Red (Basic) indicating wipes a test was conducted to determine the wipes effectiveness in detecting a small amount of residual propellant liquid from a surface
- The surface of several 3" x 2" stainless steel test panels were wetted using a swatch of the material saturated with AF-M315E or deionized water and then wiped using the indicating wipes
 - As can be seen in the images, the wipes performed similarly to the drop test, showing a vivid color change upon direct exposure to the residual AF-M315E (Figure 39c). The deionized water control sample showed no change upon exposure, indicating that the indicating wipes are not susceptible to false positives from moisture.



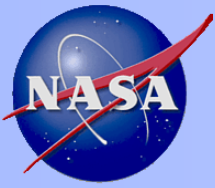
Methyl Red (Basic) Wipe Residue Test –
a) pre-exposure,
b) AF-M315E Test Panel,
c) post-exposure (AF-M315E),
d) post-exposure (DI H₂O).



Ammonium Dinitramide – ADN

- **Primary component of LMP-103S**
 - 60%-65% is ADN
- **“Green” Monopropellant LMP-103S**
 - Produced by Swedish Space Corporation (ECAPS)
 - Successfully used in 2010 PRISMA mission
 - Participant in F-16 Emergency Power Unit (EPU) test with Marshall Space Flight Center (MSFC)





COTS Sensors – Actively Pumped

- **Multi-RAE Lite**

- Active pumping
- Remote sensing
- 3 sensors
 - PID (VOC detection)
 - Catalytic Bed (combustibles)
 - Electrochemical (NH_3)
 - Wireless connectivity
 - Data logging capabilities.



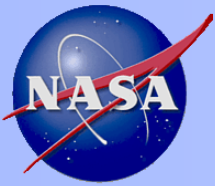
RAE Systems Multi-RAE Lite

- **Dräger X-act 5000**

- Active-pumping
- Reduces measurement time
- Variety of tubes for NH_3 detection
 - are available
 - 0.25 – 3 ppm, 0.05 – 10%,
 - 2 – 30 ppm, 5 – 600 ppm,
 - 5 – 100 ppm



Dräger X-Act® 5000



COTS Sensors – Diffusion-based

■ **GasAlert Extreme**

- Diffusion-based
- 0 – 100 ppm NH_3 sensor
- -20 - 40°C, 15 – 90% humidity
- Water resistant



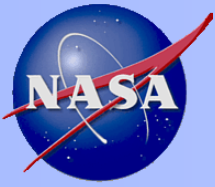
BW Technologies
GasAlert Extreme

• **Dräger Pac® 7000**

- Diffusion-based
- 0 – 300 ppm NH_3 sensor
- -40 - 40°C, 700 – 1300 mbar
- Water resistant

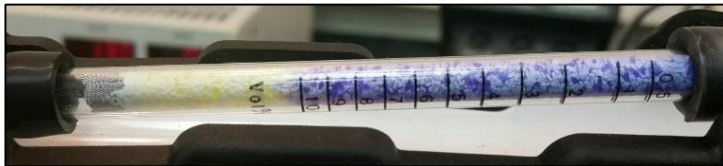


Dräger Pac® 7000

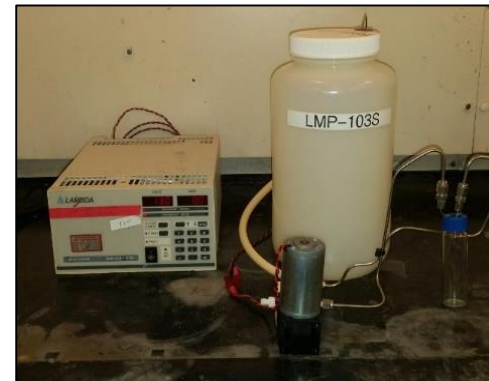


Test Results – Actively Pumped

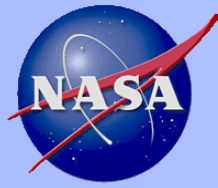
- **RAE Systems MultiRAE Lite**
 - All three sensors (catalytic bed, ammonia, and PID) of the MultiRAE unit showed extremely high and rapid response when exposed to LMP-103S
 - Three individual tests were run (although the last was shortened due to sensor saturation and the suspected possibility of damaging the electrochemical ammonia sensor)
- **Dräger X-act® 5000 (with Dräger-Tube®)**
 - A positive response was observed when exposed to LMP-103S
 - The Dräger-Tubes® that were evaluated were the 5 – 600 ppm Ammonia Tube and the 0.05 – 10% Ammonia Tube
 - The 0.05 – 10% was the primary Dräger-Tube® that was evaluated due to the volatile nature of the propellant and the very high readings of ammonia previously observed using the MultiRAE Lite multigas sensor evaluation



Results from 0 – 10% Dräger-Tube® Evaluation

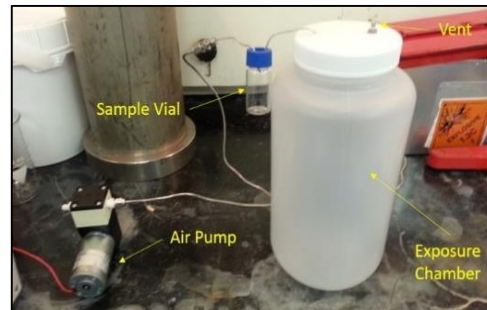


Setup for
Evaluation of
Active Sensors

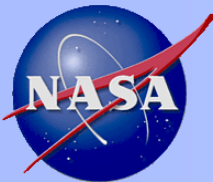


Tests Results – Diffusion Based

- **GasAlert Extreme**
 - More consistent in the response upon exposure to the LMP-103S
 - Response was very rapid in all three exposure tests (less than 15 seconds)
 - Time for the system to return to baseline was quite long, taking over three hours
 - In addition to the results described above, the masses of each sample tested were monitored pre- and post-exposure in an attempt to determine the mass loss of propellant during each sample run.
- **Dräger X-act® 7000 (with Dräger-Tube®)**
 - A positive response was observed when exposed to LMP-103S
 - This testing was done in concert with the testing of the GasAlert Extreme.
 - As compared to the other passive gas sensor (GasAlert Extreme) the reproducibility of the Dräger Pac® 7000 seemed less consistent as that the time for the system to alarm varied considerably
 - The Dräger Pac® 7000 still responded very quickly (all tests within 1 minute). The time for the system to return to baseline was also quite long, taking over three hours



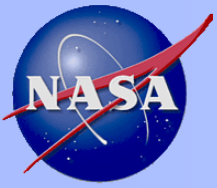
Setup for
Evaluation of
Diffusion-based
Sensors



Safety Considerations

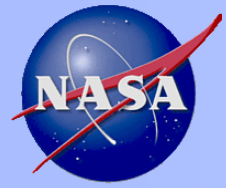
- **Hydroxylammonium Nitrate (HAN) based Monopropellant AF-M315E**
 - Safety glasses with side shields covered by a face shield
 - Nitrile rubber gloves
 - Flame retardant lab coat or coveralls

- **Ammonium Dinitradmide (ADN) based Monopropellant LMP-103S**
 - Safety glasses with side shields with half-face respirator equipped with an organic cartridge
 - Alternative – full-face respirator equipped with an organic cartridge
 - Nitrile rubber gloves



Conclusions

- **Hydroxylammonium Nitrate (HAN) based Monopropellant AF-M315E**
 - Traditional vapor sensors ineffective
 - Colorimetric detection system developed
 - Absorbent “socks” and wipes prepared
 - Vacuum-sealed to keep prevent CO₂ absorption
- **Ammonium Dinitradmide (ADN) based Monopropellant LMP-103S**
 - Vapor sensors effective (both active and diffusion-based)
 - MultiRAE Lite and GasAlert Extreme best performing
 - Stainless steel sensor wand added to MultiRAE Lite for remote sensing

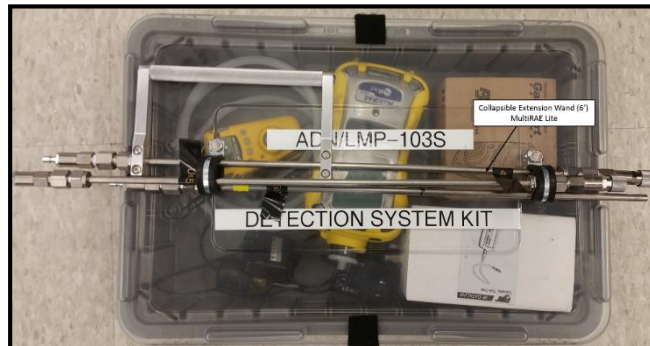


Conclusions

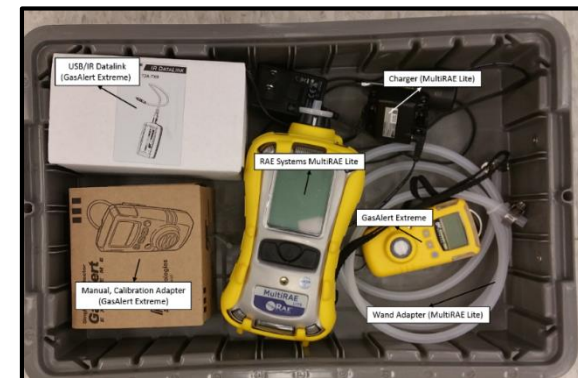
- Detection Kits developed for both “green” monopropellants



Exterior of HAN/AF-M315E Kit



Exterior of ADN/LMP-103S Kit



Interior of ADN/LMP-103S Kit



And so...

